

## INTERFEROMETRIC EVALUATION OF ASSOCIATION EQUILIBRIUM IN THE CELLULOSE ACETATE/ACETONE/WATER TERNARY SYSTEM

Adina Maria NECULA, Liliana OLARU, Niculae OLARU, Silvia IOAN

“Petru Poni” Institute of Macromolecular Chemistry, Iasi, 700487, Romania  
Corresponding author: Silvia Ioan, E-mail: ioan\_silvia@yahoo.com

The paper studies the conformational modifications of cellulose acetate with a 2.21 substitution degree, in 85/15, 90/10 and 95/5 v/v acetone/water solvent mixtures. The behavior is influenced by the preferential adsorption of acetone, which was evaluated from interferometer data. The miscibility of the ternary system is attained by competitive specific interactions between the solvent-solvent and solvent-polymer systems, which determine the compositional modification of solvent mixtures both inside and outside the polymer coil. Thus, the preferential adsorption presents a maximum value at a 0.90 volume fraction of acetone, when the dimension of the polymer chain also presents a maximum value. The intermolecular interactions observed in the cellulose acetate solution assure the primordial properties necessary for obtaining superior membranes in biomedical applications.

*Key words:* Cellulose acetate; Solution properties; Intermolecular interactions.

### 1. INTRODUCTION

The increasing need of materials for new applications requires polymers with diverse architectures, inducing specific properties. As known, solvents are essential in the modification of the dilute-solution behavior (association, complex, micelle, and core-shell structure of polymer chains in solution) of cellulose derivatives. Light scattering, interferometry and viscometric measurements are the simplest methods of assessing their properties in solution [1,2]. Preferential adsorption coefficients, which indicate the modification of the mixed solvent composition in vicinity of the polymer chain, were directly accessible from the experiments, through interferometry. Also, intrinsic viscosity, viscosity slope coefficient, and Huggins constant,  $K_H$ , for the viscosity behavior are common parameters characterizing the dilute-solution properties of a cellulose acetate with different substitution degrees, while the Huggins constant is the theoretical representation of the thermodynamic and hydrodynamic properties. Therefore,  $K_H$  could thermodynamically reflect the nature of the solvent, the interaction between the cellulose acetate chain and solvent. Extensive studies have been conducted on the effect of the used solvents on the morphology and performance of these polymers in different applications, such as ultrafiltration membranes [3-5], reverse-osmosis membranes [6], gas-separation membranes [7], and pervaporation membranes [8,9]. Addition of a second solvent (which is mostly a nonsolvent [10]) to the casting solution is often used for increasing the permeation flux of a membrane.

Literature data [9] have pointed out that the structures, boiling point, content of the mixture solvents, or intrinsic viscosity, affect the performance of some applications. In the present study, the conformational behavior and unperturbed dimensions of cellulose acetate with a 2.21 substitution degree were investigated by viscometry and interferometry, in acetone/water solvent mixtures. The influence of concentration and temperature on coil densities and dimensions, as well as the influence of solvent mixtures, composition on the solution properties were also discussed.

## 2. EXPERIMENTAL

Cellulose acetate with a 2.21 substitution degree (CA2.21) and with number average molecular weight  $M_n = 40000$  has been synthesized in conventional (acetic acid/water) media [11,12].

Viscosity measurements were carried out in 85/15, 90/10 and 95/5 v/v acetone (1)/water (2) mixtures, over the 20°C-50°C temperature range ( $\pm 0.01^\circ\text{C}$ ), on an Ubbelohde suspended-level viscometer. The measurements were performed within one day after the samples were brought into solution within 5 h. The concentration range was of 0.4 – 1.3 g/dL. The kinetic energy corrections were negligible. The flow volume of the used viscometer exceeded 5 mL, making drainage errors unimportant. Flow times were obtained with an accuracy of approx. 0.035 % in different measurements of the sample in acetone/water, at a given temperature. Huggins and Rao equations were used to evaluate intrinsic viscosity,  $[\eta]$ :

$$\eta_{sp} / c = [\eta] + k_1 \cdot [\eta]_{Huggins}^2 \cdot c \quad (1)$$

$$\frac{1}{2(\eta_{rel}^{1/2} - 1)} = \frac{1}{[\eta]_{Rao} c} - \frac{(a-1)}{2.5} \quad (2)$$

where  $\eta_{sp}$  is specific viscosity,  $k_H$  is the Huggins constant,  $c$  is the concentration of polymer solution,  $a = 1/\Phi_m$ , and  $\Phi_m$  is the maximum volume fraction to which the particles can pack, expressed by  $\Phi_m = \frac{[\eta]}{2.5} \cdot c_m$ .

The preferential adsorption coefficients,  $\lambda_1$ , were directly accessible from the experiments, through interferometry (Zeiss interferometer) at 25°C and dialysis equilibrium, according to equation (3):

$$\lambda_1 = \frac{(dn/dc)_\mu - (dn/dc)_u}{dn_0/d\phi_1} \quad (3)$$

where  $(dn/dc)_u$  and  $(dn/dc)_\mu$  are the refractive index increments of the polymer in acetone/water solvent mixtures, before and after establishing dialysis equilibrium, respectively, and  $dn_0/d\phi_1$  is the variation of the refractive index increment of the solvent mixture as a function of acetone volumetric composition.

Equilibrium dialysis experiments of the cellulose acetate (3) in acetone (1)/water (2) mixed solvents were carried out in a dialyser with a total volume of about 15 mL. Before use, the semipermeable cellophane membrane was conditioned in each of the solvent mixtures. Dialysis equilibrium was obtained within 6 h.

## 3. RESULTS AND DISCUSSIONS

### 3.1. Influence of solvent mixtures and temperatures on the cellulose acetate with a 2.21 substitution degree

Special mention should be made of the fact that viscometry represents, probably, the most widely used experimental method to assess the conformational modification of polymers in solution. Indeed, viscometric behaviors are related to the chemical structure of the cellulose acetate, to its size, and also to environmental properties such as interaction appearing in mixed solvents.

Figure 1 shows the Huggins and Rao plots for CA2.21 in a 90/10 acetone/water solvent mixture, at 20°C.  $[\eta]_{Rao}$  is higher than  $[\eta]_H$  by about 4 %; anyway, this error is within the limit accepted by the methods used to calculate intrinsic viscosity. Also, the Huggins constants values,  $K_H$ , of 1.8, 1.5 and 1.6 for 0.85, 0.90 and 0.95 volume fraction of acetone, respectively, prove the existence of aggregation in solution, especially for extreme compositions of the studied mixed solvents. The  $K_H$  value of the polymer solution is an important variable governing the morphology and performance of cellulose membranes. The reason could be that chain association in a polymer solution results in macromolecular aggregates in the membranes, ultimately bringing about different cellulose performances of the membranes [9]. That is why, the values of

intrinsic viscosity utilized in this work are obtained by the Rao method (expressed by equation (2)), characterized by a higher precision according, to Figure 1. Intrinsic viscosities and their dependence on temperature are shown in Figure 2 for 85/15, 90/10 and 95/5 v/v acetone/water solvent mixtures. The obtained linear dependencies, showing negative slopes, have been interpreted in terms of a conformational change of the polymer chain. These results seem to indicate that the main factor of solvation power is solvents polarity, and their interactions with the cellulose acetate. Literature [13,14,] shows that the excess molar enthalpy of the studied mixed solvent is negative, indicating that the strength of the water–acetone hydrogen bond is higher than that of the water–water hydrogen bond. Information about the strength of the water–acetone hydrogen bond was obtained by analyzing the measurements with a quasi-chemical association model. This phenomenon determines important changes in the structure of the solvents responsible for the changes occurring during the solvation of polymer. Thus, the acetone/water 90/10 v/v dissolves better CA2.21 than the mixed solvent acetone/water 85/15 v/v and 95/5 v/v.

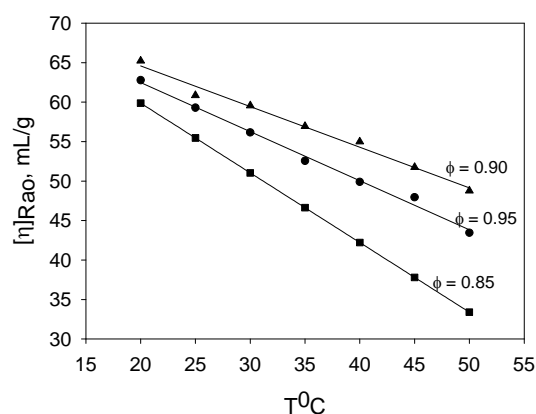


Figure 2. Rao plots for CA2.21 in different compositions of an acetone/water mixture, at different temperatures

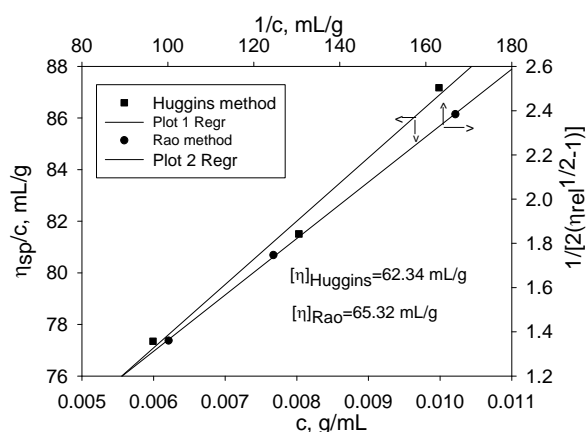


Figure 1. Huggins and Rao plots for CA2.21 in a 90/10 acetone/water solvent mixture at 20°C

The values of intrinsic viscosity are affected by the different interactions from the system. Figure 3 illustrates the variation of intrinsic viscosity with the volume fraction of acetone in acetone/water mixture.

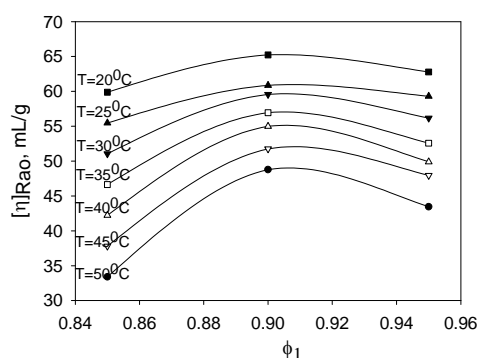


Figure 3. Intrinsic viscosity vs. volume fraction of acetone for cellulose acetate with a 2.21 substitution degree in acetone/water mixtures, at different temperatures

Polymer's coil dimension is seen as increasing, attaining a maximum value at a 0.90 volume fraction of acetone, for all studied temperatures. The sample precipitates at volume fractions of acetone below 0.85 and over 0.95. Thus, the precipitation is due to the competition between the association phenomena occurring in the used solvents and their interactions with the polymer.

### 3.2. Conformational properties of cellulose acetate with a 2.21 substitution degree in solution

The influence of solvent mixtures on the conformational properties of cellulose acetate in dilute solution was estimated by the Qian and Rudin method [15-17]. Thus, coil density,  $\rho$ , of the polymer chains in solution was determined by viscosity measurement, as follows:

$$\rho = \frac{c}{\eta_{sp}} \left( 1.25 + 0.5 \sqrt{56.4 \eta_{sp} + 6.25} \right) \quad (4)$$

or

$$\rho = \frac{c^*}{0.77^3} \left\{ 1 + \frac{[\eta] - [\eta]_0}{[\eta]_0} \left[ 1 - \exp\left(-\frac{c}{c^*}\right) \right] \right\} \quad (5)$$

Here,  $c^*$ , the critical concentration at which the polymer coils begin to overlap on each other, is defined by equation (6), and  $[\eta]_0$  is the intrinsic viscosity in unperturbed state, defined by equation (7) :

$$c^* = \frac{0.77}{[\eta]} \quad (6)$$

$$[\eta]_0 = \frac{[\eta] \left[ 1 - \exp\left(-\frac{c}{c^*}\right) \right]}{\frac{0.77^3 \rho}{c^*} - \exp\left(-\frac{c}{c^*}\right)} \quad (7)$$

Figures 4 and 5 show the concentration dependence on coil density for cellulose acetate, in 0.90 and 0.95 volumes fractions of acetone, in the dilute range, as well as for a large concentration domain. The small plot corresponds to experimental data in dilute solution.

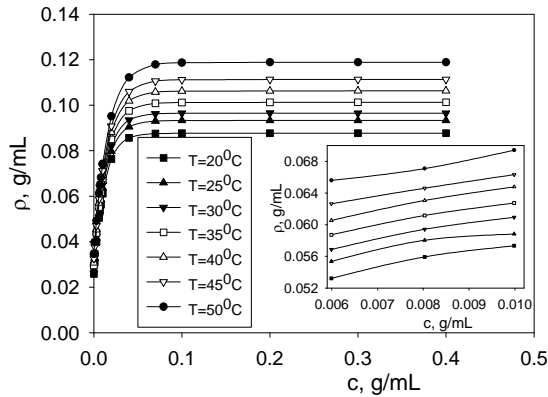


Figure 4. Variation of coil density with concentration for cellulose acetate with a 2.21 substitution degree in a 0.90 volume fraction of acetone. The small plot corresponds to experimental data in dilute solution

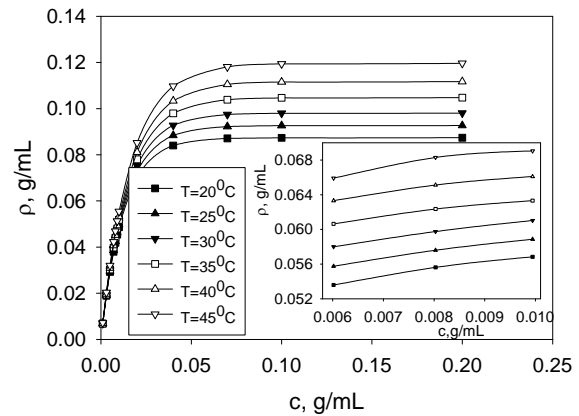


Figure 5. Variation of coil density with concentration for cellulose acetate with a 2.21 substitution degree in 0.95 volume fraction of acetone. The small plot corresponds to experimental data in dilute solution

The polymer coil density increases with increasing polymer concentration while, at a critical concentration from the semidilute domain,  $c^+$ , coil density remains constant. Thus, the density at  $c \geq c^+$  corresponds to the density on unperturbed state. Modification of coil density is reflected in the variation of the gyration radius with concentration, evaluated by equation (8) .

$$R_g^3 = \frac{3M[\eta]}{3\phi \left\{ 1 + \frac{[\eta] - [\eta]_0}{[\eta]_0} \left[ 1 - \exp\left(-\frac{c}{c^*}\right) \right] \right\}} \quad (8)$$

The dependencies between these dimensions and concentration were presented in Figures 6 and 7 for cellulose acetate, in 0.90 and 0.95 volume fractions of acetone, respectively. The small plot corresponds to experimental data in dilute solution.

The radii of gyration decrease with increasing concentration while, at critical concentration  $c^+$  (identical values with those from Figures 4 and 5) they are considered to shrink to their unperturbed dimensions. Thus, the radius of gyration at  $c \geq c^+$  corresponds to the radius of gyration in unperturbed state. The critical concentrations  $c^+$ , are approximated by  $c^+ \cong 8c^*$  [15,16]. For exemplified, the critical concentrations  $c^*$  and  $c^+$  are delimited in Figure 7 for different temperatures.

The thermodynamic parameters represented by the gyration radii in perturbed,  $R_{g,c=0}$ , and unperturbed state,  $R_{g,c=0}$  (evaluated from Figures 6 and 7), intrinsic viscosity in unperturbed state (evaluated from equation (7)),  $[\eta]_0$ , and the unperturbed dimension parameters,  $K_\theta$ , (calculated from equation (9)) for cellulose acetate in 0.90 and 0.95 volume fractions of acetone, at different temperatures, are summarized in Tables 1 and 2.

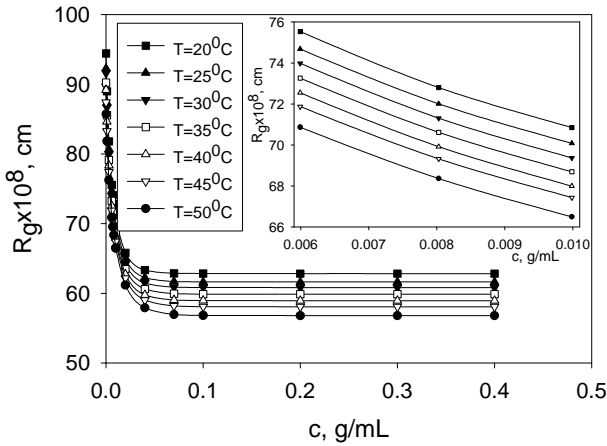


Figure 6. Variation of the gyration radius with concentration for cellulose acetate with 2.21 substitution degree in a 0.90 volume fraction of acetone. The small plot corresponds to experimental data in dilute solution

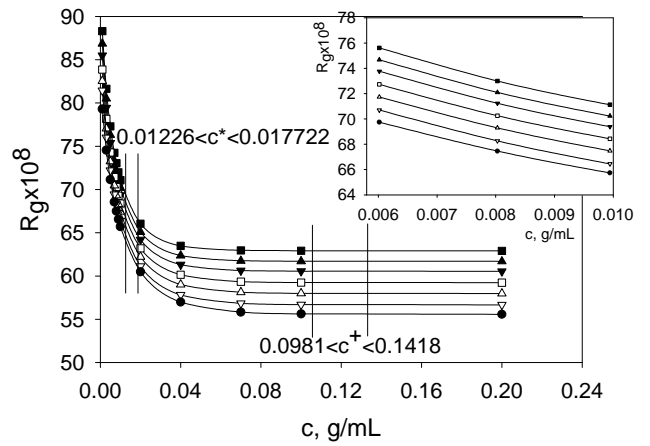


Figure 7. Variation of gyration radius with concentration for cellulose acetate with a 2.21 substitution degree, in a 0.95 volume fraction of acetone. The small plot corresponds to experimental data in dilute solution: (■) – 20°C; (▲) – 25°C; (▼) – 30°C; (□) – 35°C; (Δ) – 40°C; (▽) – 45°C; (●) – 50°C

The values obtained for the unperturbed dimension parameters, reflecting the influence of solvent mixture and temperature, are comparable with literature data [18]. Inconclusive results were obtained for  $[\eta]_0$  in a 0.85 volume fraction of acetones, as due to the existence of pronounced polymer aggregations phenomena in solution. Dependence of the temperature coefficient,  $\ln[\eta]/T$ , on the volume fraction of solvent mixtures confirms this conclusion. Thus, the values of  $-\frac{d \ln[\eta]}{dT}$  are of 0.01930, 0.00912, 0.01177 for 0.85, 0.90 and 0.95 volume fractions of acetone, respectively. Higher values of temperature coefficients, at a 0.85 and 0.95 volume fraction of acetone, could be caused, according to literature data [1,2], by partial dissociation of the polymer.

$$K_\theta = [\eta]_0 / M^{0.5} \quad (9)$$

Also, Tables 1 and 2 show that conformation of the polymer chains is modified by the temperature and volume fraction of the solvent mixtures. The coil dimension in perturbed and unperturbed state increases with increasing the acetone content, attaining a maximum value at a 0.90 volume fraction of acetone. Moreover, it is observed that, for volume fractions of acetone over 0.95 and below 0.85, the sample precipitates (as confirmed by viscometric data, as well).

Table 1. Perturbed and unperturbed gyration radius (cm), intrinsic viscosity in unperturbed state (mL/g) and unperturbed dimension parameter ( $\text{mL mol}^{1/2}/\text{g}^{3/2}$ ) at different temperatures, for cellulose acetate, in a 0.90 volume fraction of acetone

$T, ^\circ\text{C}$	$R_{g,c=0} \cdot 10^8$	$R_{g,c=\theta} \cdot 10^8$	$[\eta]_\theta$	$K_\theta$
20	94.41	62.83	19.22	0.0961
25	92.26	61.63	18.14	0.0907
30	91.60	60.82	17.43	0.0872
35	90.24	59.87	16.63	0.0832
40	89.19	58.94	15.87	0.0793
45	87.40	58.06	15.17	0.0759
50	85.70	50.80	14.20	0.0710

Table 2. Perturbed and unperturbed gyration radius (cm), intrinsic viscosity in unperturbed state (mL/g) and unperturbed dimension parameter ( $\text{mL mol}^{1/2}/\text{g}^{3/2}$ ), at different temperature, for cellulose acetate in a 0.95 volume fraction of acetone

$T, ^\circ\text{C}$	$R_{g,c=0} \cdot 10^8$	$R_{g,c=\theta} \cdot 10^8$	$[\eta]_\theta$	$K_\theta$
20	93.22	62.92	19.30	0.0965
25	91.46	61.70	18.20	0.0910
30	89.82	60.55	17.20	0.0860
35	87.86	59.23	16.10	0.0805
40	86.35	57.97	15.10	0.0755
45	85.21	56.66	14.10	0.0705
50	82.46	55.57	13.30	0.0665

### 3.3. Preferential adsorption

Figure 8 illustrates the variation of the preferential adsorption coefficient,  $\lambda_1$ , with the acetone content, for CA2.21, in the acetone (1)/water (2) binary mixture experimentally determined from refractive index increments, both before  $\left(\frac{dn}{dc}\right)_u$  and after  $\left(\frac{dn}{dc}\right)_\mu$  establishing dialysis equilibrium (Table 3) from equation (3). The value of  $dn/d\phi_1 = 0.026$  for the acetone/water system, evidencing an ideal behavior across the whole composition range investigated (0-100%), obtained from the derivation of linear dependencies expressed by equation (10), is also listed in Table 3.

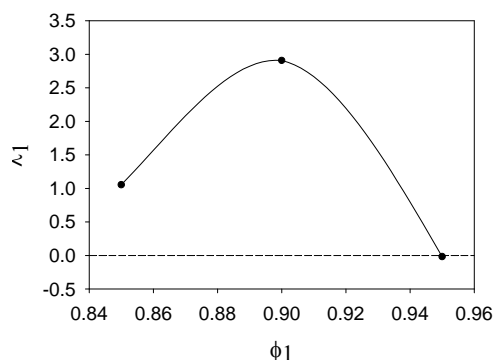


Figure 8. Experimental values of the preferential adsorption coefficient for CA2.21 vs. the volume fraction of acetone at 25°C.

**Table 3. Specific refractive index increments before,  $\left(\frac{dn}{dc}\right)_u$ , and after,  $\left(\frac{dn}{dc}\right)_\mu$ , establishing dialysis equilibrium for CA2.21 in acetone/water binary solvent mixtures, as a function of the acetone content,  $\phi_1$ , and the refractive index increment of the solvent mixture,  $\frac{dn}{d\phi_1}$**

$\phi_1$ (acetonă)	$\left(\frac{dn}{dc}\right)_u$	$\left(\frac{dn}{dc}\right)_\mu$	$\frac{dn}{d\phi_1}$
0,85	0,08548	0,11299	0,026
0,90	0,09759	0,17318	0,026
0,95	0,11322	0,11279	0,026

$$n = 1.330 + 0.029 \cdot \phi_1 \quad (10)$$

where  $n$  is the refractive index of the mixed solvents. In this system, the experimental results indicate that preferential adsorption is markedly influenced by the competitive influence of association phenomena of both the solvents used and of their interaction with CA2.21.

According to Figure 8, acetone and water are non-solvents for the cellulose acetate with a 2.21 substitution degree, but their mixture becomes a good solvent in a 0.85 – 0.95 volume fraction of the acetone domain. Here, acetone is preferentially adsorbed ( $\lambda_1$  shows positive values) and, at  $\phi_1 = 0.85$  and  $0.95$ , the preferential adsorption coefficient has minimum values, which reveals its same affinity for both solvents. Moreover, the above mentioned association phenomenon changes the solubility of CA2.21, determining modification of  $[\eta]$  and  $\lambda_1$ .

Consequently, three distinct ranges of acetone composition, in which the solvent mixture will have very different interactive properties have been evidenced. Therefore, the polymer chains exhibit the tendency to surround themselves with the thermodynamically most efficient solvent, at a given composition of the solvent mixture.

#### 4. CONCLUSION

Modification of intrinsic viscosity and of the preferential adsorption coefficients of cellulose acetate with a 2.21 substitution degree in acetone/water non-solvent mixtures was investigated. These solutions are characterized by the existence of association phenomena of both solvents, *i.e.*, acetone and water, and poor solvation of this polymer in different solvents. In this context, the Huggins constants show the existence of aggregation in solution, especially for extreme compositions of the studied mixed acetone/water non-solvents.

Polymer's the intrinsic viscosity increases and decreases with increasing the acetone content. Also, the linear dependencies with negative slope for intrinsic viscosity *vs.* temperature for all volume fraction of acetone, were obtained. These behaviors indicate the thermodynamic quality of the solvent mixtures. Thus, modifications of intrinsic viscosity and of temperature coefficients have been interpreted in terms of a conformational change of the polymer chain, of association phenomena corresponding to both solvents, and of an aggregation trend of cellulose acetate in mixed solvents, transmitted to the coil density, to the unperturbed dimension parameters and to the preferential adsorption coefficients values.

With increasing concentrations, the density of the polymer coil increases and the dimensions decreases. At a critical concentration from the semidilute domain, the density and dimension of the polymer coil are considered to shrink to their unperturbed dimensions.

The unperturbed dimension parameters agree with literature data, being influenced by the used solvent mixtures. The values of  $\lambda_1$  show a preferential adsorption of acetone over the  $\phi_1 = 0.85 - 0.95$  composition range of acetone. Below and over these composition values, the polymer precipitates. These results are

related to the Gibbs free energy of mixing solvents, quantifying the polymer-binary solvent interaction by intrinsic viscosity.

The high intermolecular interactions observed in the cellulose acetate solution constitute the main properties for obtaining superior membranes for hyperfiltration applications.

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